

COAL LIQUEFACTION WITH TIN OXIDE CATALYST

M. Mizumoto, H. Yamashita, and S. Matsuda
Hitachi Research Laboratory
Hitachi Ltd.
Ibaraki, Japan 31912

INTRODUCTION

In recent years, a large amount of work has been performed in the region of coal chemistry. Liquefaction of coal has been investigated widely not only of industrial application but also fundamental interests. Various catalysts are examined in a huge amount of papers reported. They are classified into many categories. One of them is metal oxide catalyst. Metal oxide catalysts are easily prepared and handled. Iron oxide catalyst and HDS catalyst have been tested in pilot scale experiments. In this paper, we examined the catalytic activity of metal oxide catalysts for direct liquefaction of coal.

It is useful to investigate the mechanism of the liquefaction of coal using model compounds which are typical of coal. In the latter part of this paper, we examine the hydrogenation of benzyl ether and discuss the reaction path of liquefaction.

EXPERIMENTAL SECTION

Figure 1 shows the experimental apparatus used in this work. The autoclave was made of stainless steel. Coal or model compounds were mixed with solvent and catalyst in the autoclave by continuous stirring. The autoclave was heated up to reaction temperature at a rate of 50°C/min under pressurized hydrogen.

Liquid products were separated into three fractions by solvent extraction. That is, n-hexane soluble fraction was called oil, n-hexane insoluble and toluene soluble fraction was called asphaltene, and toluene insoluble fraction was called residue. Conversion of coal was calculated from the weight of residue (daf). Gas chromatography was used for analysis of gas and liquid products. Residue was analyzed by X-ray diffraction.

The composition of coals used in this work is shown in Table 1. Powdered coal (0.1 - 0.4 mm) was mixed with twofold of creosote oil. Catalysts were prepared by the following methods. That is, calcination of hydroxide (Fe_2O_3 , TiO_2 , MnO , ZnO , SnO_2) and impregnation method ($\text{Co-Mo-Al}_2\text{O}_3$, Ni-Mo-TiO_2). Powdered catalyst passed through a 200 mesh sieve was mixed with slurry in a ratio of 5 wt% to coal. Benzyl ether, phenyl ether, and dibenzyl were used as model compounds. They were added to 1-methylnaphthalene (MN) or tetralin and hydrogenated in the presence or absence of SnO_2 catalyst.

RESULTS AND DISCUSSION

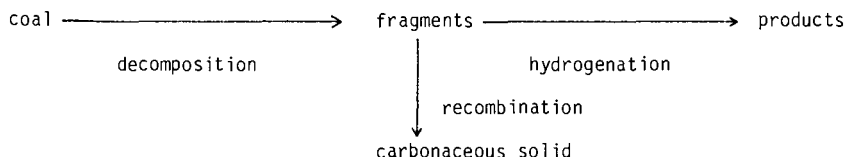
Coals were liquefied at 450°C for 30 min under pressure of 150 atm. Pressurized hydrogen was allowed to flow at a rate of 300 l/hr (stp).

Figure 2 shows the conversion of Taiheiyo coal liquefied with various catalysts. It was found that SnO_2 catalyst showed the highest activity, and that the conversion of coal and yield of oil reached 100% and 75%, respectively. Consequently the reactions with SnO_2 catalyst were examined in detail hereafter.

At first, three kinds of coal were liquefied with SnO_2 catalyst under the same conditions mentioned above. Conversion of coal is shown in Figure 3. It was found that the conversion of coal increases with the content of volatile matter.

It was found that catalyst distributed in residue was reduced to metallic tin from X-ray diffraction analysis. Therefore it was considered that catalyst present in coal mixture under reaction conditions is melted tin metal.

The following scheme is well-known as the reaction path for coal liquefaction.



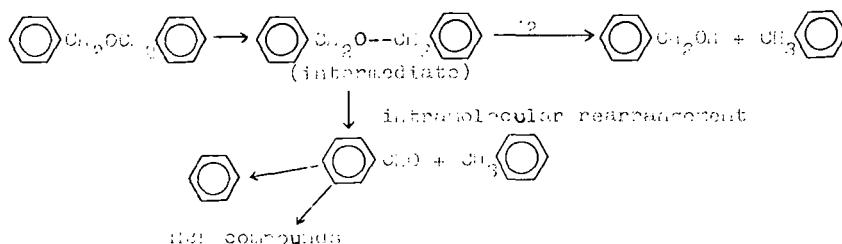
Scheme I

Coal is thermally decomposed to fragments followed by hydrogenation and recombination reactions. Fragments were recombined with each other to form carbonaceous solid which is one of the components of residue. When SnO_2 was used as catalyst, residue was not formed. It is considered that SnO_2 has higher selectivity for hydrogenation than for recombination. In order to confirm the reason we examined the hydrogenation of model compounds.

Benzyl ether was hydrogenated with or without SnO_2 catalyst under initial pressure of 150 atm. Figure 4 shows the gas chromatograms of products hydrogenated at 350°C in 1-methylnaphthalene. There are some differences in product distribution. In the presence of SnO_2 catalyst, benzyl ether decomposed to toluene and benzyl alcohol. Compounds which have higher boiling points than benzyl ether (called HBP compounds) such as fluoranthene were formed at low selectivity. On the contrary, the selectivity to HBP compounds increased in the absence of SnO_2 catalyst. Products from hydrogenation of benzyl ether with several catalysts are shown in Table 2. The selectivity to HBP compounds was found to be about 40% without SnO_2 catalyst, while in the presence of SnO_2 about 10%. It was also found that the selectivity was independent of the hydrogen donating property of solvent.

Phenyl ether and dibenzyl were hydrogenated under the same conditions. Compared with benzyl ether, conversions of them were low due to higher bond energy.

It was deduced that decomposition of benzyl ether takes place by the following scheme from the results of this work.



Scheme II

Benzyl ether decomposed to benzaldehyde and toluene accompanied with intra-molecular rearrangement of hydrogen without SnO_2 catalyst. Benzaldehyde decomposed consecutively to benzene and reacted with solvent molecule to form HBP compounds such as fluoranthene. On the contrary, the reaction path seems to be different in the presence of SnO_2 catalyst. It was considered that the rate of hydrogenation of intermediate becomes higher than that of rearrangement with SnO_2 . Therefore benzyl ether decomposed to toluene and benzyl alcohol with low selectivity to HBP compounds.

In this paper we discussed the reaction path of hydrogenation of coals and model compounds. It was concluded that tin interacts with fragments of coal and stabilized fragments to prevent recombination reaction.

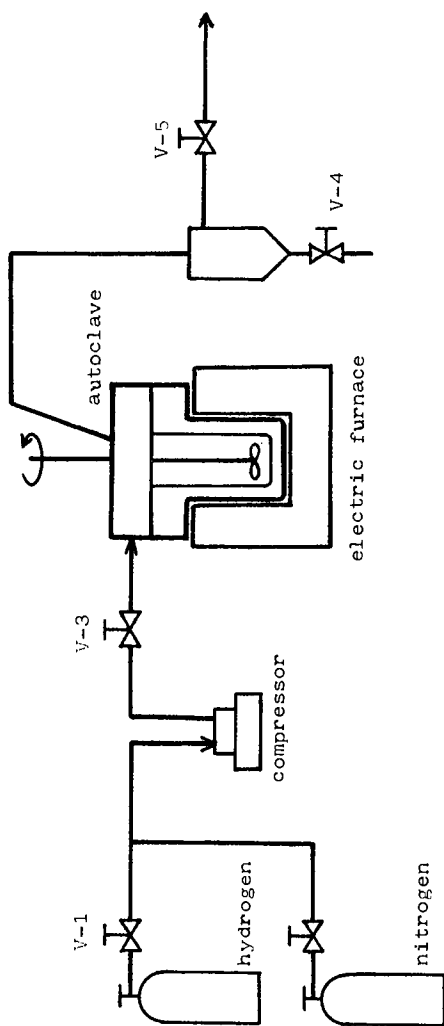


Figure 1. Experimental apparatus

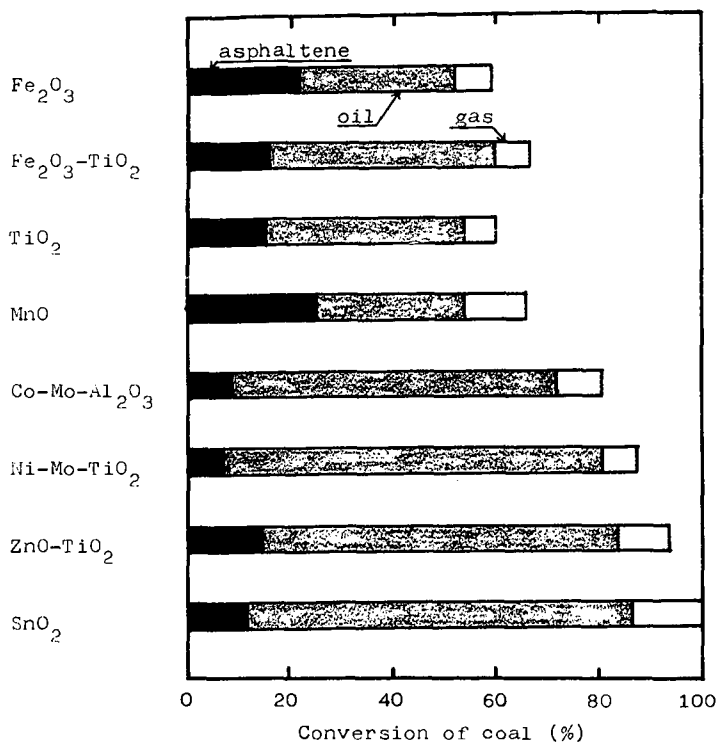


Figure 2. Liquefaction activity of catalysts.
 reaction temperature; 450 C, reaction time;
 30min, H_2 pressure; 150atm

Table 1. Composition of coal.

coal	proximate analysis (%)				ultimate analysis (%)		
	ash	moisture	v.m.	f.c.	C	H	N
Taiheiyō	13.9	5.1	43.8	37.2	63.9	5.6	1.1
Mi-ike	16.2	2.6	37.2	44.0	68.3	5.0	1.1
Da tong	9.7	1.9	23.9	59.5	77.5	4.6	0.9

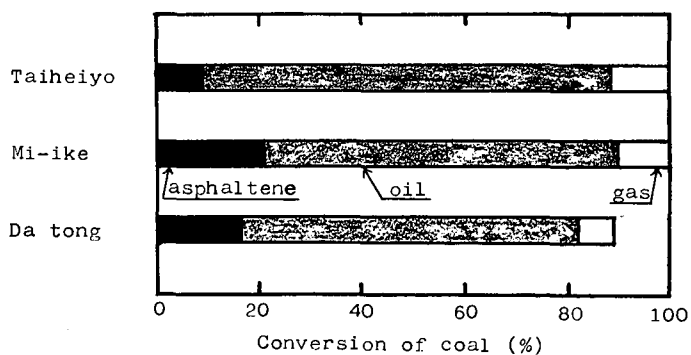


Figure 3. Reactivity of coal with SnO₂.
 reaction temperature; 450°C, reaction time;
 30min, H₂ pressure; 150atm

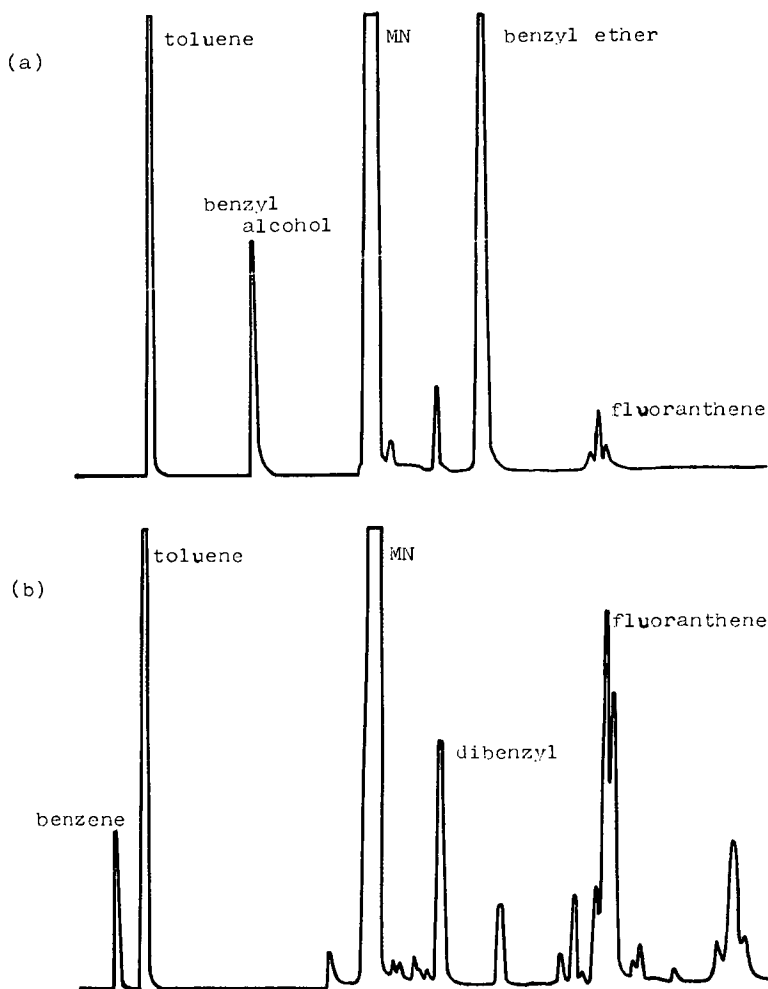


Figure 4. Gaschromatograms of products from hydrogenation of benzyl ether (a) with SnO_2 , (b) without SnO_2 . reaction temperature; 350°C , reaction time; 30min, initial H_2 pressure; 150atm

Table 2. Products from hydrogenation of benzyl ether.

catalyst	solvent	selectivity (%)			
		benzene	toluene	benzyl alcohol	HBP compounds §§
no	MN §	4.7	57.0	0	38.3
	tetralin	2.4	55.8	0	41.8
Ni-Mo-TiO ₂	tetralin	9.9	45.6	0	44.5
SnO ₂	MN	0	51.6	38.4	10.1

§ 1-methylnaphthalene

§§ compounds whose boiling points are higher than benzylether

A STRUCTURAL INVESTIGATION OF THE EFFECT OF CATALYSIS
ON THE LIQUEFACTION PRODUCTS OF A BROWN AND
A BITUMINOUS AUSTRALIAN COAL

M.G. Strachan,^A A.M. Vassallo^B and R.B. Johns^A

- A. Department of Organic Chemistry, University of Melbourne,
Parkville, Victoria, Australia 3052.
B. C.S.I.R.O. Division of Fossil Fuels, North Ryde, N.S.W.,
Australia 2113.

INTRODUCTION

The effect of catalysts on the donor solvent hydrogenation of Australian coals, both brown and black, have been investigated by a number of workers (1-5). However, these studies have concentrated mainly on obtaining conversion, oil yield, asphaltene and preasphaltene data, rather than emphasising chemical structural analysis of the resultant products. To solely use the forementioned criteria as a basis for catalyst evaluation can and may be misleading, as the product quality is an unknown parameter, which can give much insight into both the effectiveness and mechanism of catalysis.

The paper reports a study comparing the effects of a single catalyst, Co/Mo, on two Australian coals of different rank at their uncatalyzed optimal oil yield temperatures (4)(8)(9) under donor solvent conditions. It was considered more appropriate to compare the products from the two coals at their respective optimal oil yield temperatures rather than at the same temperature. The former accounts and compensates for differing thermal reactivities with rank, thereby allowing a direct comparison of product qualities to be made.

The coals used for the study were a Victorian brown coal, LY1277, from the Loy Yang Field, a medium-light lithotype, and a N.S.W. high volatile bituminous coal from the Liddell Field. They were chosen because of their known liquefaction potential. They were reacted at 375°C and 425°C respectively, in batch autoclaves using a solvent (tetralin) coal ratio of 2:1, a catalyst concentration of 10% w/w coal and were reacted for 2 hours at temperature.

The total liquid product (TLP) (defined as CH_2Cl_2 solubles) was fractionated by a separation method (6) designed specifically to separate by functionality into chemically defined classes viz. acids, bases and neutrals. This method utilizes a sequence of ion-exchange resins and silica adsorption chromatography. A feature of the method is that it does not remove the donor solvent until all the polar material is absent, hence alleviating the risk of thermal alteration of the samples as may occur with an initial dissolution step. The method is very effective in class separation.

The TLP, residues and the resulting fractions have been investigated by a number of analytical and spectroscopic methods in an attempt to use chemical analysis as a probe for investigating the effectiveness, mode of action, and structural dependence of the catalyst. Although the TLP has been fractionated into its component classes the majority of the data reported here concerns mainly the TLP and residue.

RESULTS AND DISCUSSION

The effect of the Co/Mo catalyst on the two coals, as judged by normal liquefaction criteria is shown in Table 1. In both cases conversion increased with catalysis,

however the oil yields for the catalyzed (C) Liddell run was lower than for the uncatalyzed (UC), run, the converse of the Loy Yang case. The oil yield for the uncatalyzed Liddell run was much better than for both the Loy Yang runs, with the catalyzed Liddell run being only slightly lower in yield than the catalyzed Loy Yang run. On a conversion basis the catalyzed Liddell run gave 92% conversion compared to 62% for the uncatalyzed run, and 75% and 60% for the catalyzed and uncatalyzed Loy Yang runs respectively. Hence, on an oil yield/conversion basis the coals exhibit different liquefaction behaviour. Catalytic liquefaction of Liddell markedly increases conversion, but decreases oil yield. The increased conversion is at the expense of increased H₂O production and gasification. The gases being predominantly hydrocarbons. To determine the effect of catalyst, as to whether it primarily increases oil yield and/or conversion, or actually upgrades the products, the ratio of the H₂O and gases to oil yield must be taken. Clearly the ratio of H₂O/oil yield and gas/oil yield is very similar for the Loy Yang runs (Table 1), while it is markedly different between the two Liddell runs. These data indicate that in the Loy Yang runs the catalyst is not removing heteroatoms or upgrading the product, but rather interacting only with the coal and assisting its dissolution. However in the Liddell case the marked increase in the two ratios indicates both cleavage of alkyl side chains and heteroatom removal (i.e. the product is being affected by the catalyst).

Elemental analysis (Table 2) gives credence to these initial conclusions with H/C and O/C ratios being marginally higher for the uncatalyzed Loy Yang oil than the catalyzed oil, but still very similar. Whereas, the Liddell runs show the converse viz., increased H/C and much decreased O/C for the catalyzed compared to the uncatalyzed oil. Data on the oils (Table 3) shows the composition (% w/w oil) of the LY1277 oils to be very similar (similar percentages of the various acidic, basic and neutral materials). This adds further to the hypothesis that the catalyst is primarily increasing the yield of product rather than upgrading it. If the catalyst had acted on the oil it would not be unreasonable to expect differences in the composition of the oils. This is indeed shown with the Liddell oils, where the uncatalyzed oil has 75% of its material as acids and bases (25% and 50% respectively), whereas in the catalyzed oil over 75% of the material is neutral, with less than 16% being basic. It is observed that nearly 70% of the oil exists as nonpolar neutrals which are predominantly aliphatic and aromatic hydrocarbons (7), whereas in the uncatalyzed oil this fraction represents only 14%. This is in marked contrast to the LY1277 oils where their respective percentages of nonpolar neutrals is very similar, as is the percentage of polar neutrals. Obviously this data shows quite markedly that for the Liddell oils the catalyst is acting not only on the coal but also on the resultant product, upgrading it via loss of functionalities to produce hydrocarbon neutral material. This data reaffirms the trends shown by H₂O/oil yield and gas/oil yield ratios.

Spectroscopic and molecular weight data further confirms these trends. A comparison of IR spectra (Figs. 1, 2), using semi-quantitative methods reveals only a minor decrease in the -OH absorption for the catalyzed LY1277 oil, whilst there is a marked reduction in the same absorption in the catalyzed Liddell oil. This is reinforced by the analogous reduction in the H₂O as shown by ¹H nmr. The aromaticities as determined by ¹³C nmr (Fig. 3) of both catalyzed oils increased marginally over their uncatalyzed counterparts, with both the Liddell oils being much more aromatic than the LY1277 oils.

¹H nmr has shown there to be a reduction in the amount of aromatic protons (Har) for the catalyzed compared to the uncatalyzed LY1277 oil, the converse occurred for the Liddell oils (Table 4). Similarly, the percentage of methylene protons (Ho) and hence average side chain length increased for the catalyzed LY1277 oil compared to the uncatalyzed oil, whereas there was a marked reduction in both for the catalyzed Liddell oil. This is not surprising considering the high yield of

hydrocarbon gases from the latter, most probably formed from side chain cleavage. This view is further substantiated by the increase in the percentage of protons or carbons α to aromatic rings (H_α) compared to the uncatalyzed Liddell oil. However, with the catalyzed LY1277 oil there is a marked reduction in the percentage of H_α . This observation and the increase in H_o suggests that the catalyst may be operating in either of two ways: (a) hydrogenating aromatic rings or (b) enhancing the cleavage and hence ring opening of naphthenic rings in the coal structure. It is more likely the latter is occurring as the former was not observed for the Liddell oil, which also contains aromatic rings, and the structure of brown coal is suggested as having a large proportion of naphthenic rings and arene systems (10). This mode of action of the catalyst is more consistent with the other data, suggesting it is operating on the decomposition and dissolution of the coal rather than upgrading the oil. Modified Brown-Ladner equations (11) showed the LY1277 oils to both have a similar degree of substitution, whereas the Liddell oils were much lower in value with the catalyzed oil being substantially lower than that for the uncatalyzed oil. This trend is also shown by the Har/Car ratio, from both the modified Brown-Ladner method and directly from 1H and ^{13}C nmr, (cf. Table 4) where the degree of condensation is much reduced for the uncatalyzed compared to the catalyzed Liddell oil, which in turn is similar in value to the LY1277 oils.

This is suggestive of the catalyzed Liddell oil having a smaller average ring size and hence molecular weight than the other oils. Molecular weight data proves this to be the case, with the catalyzed Liddell oil having a MW less than half that of the uncatalyzed oil (169 and 379 respectively). The latter is slightly less than that found for the LY1277 oils which in turn have similar MWs (498 for the uncatalyzed and 512 for the catalyzed oil).

The semi-quantitative IR data agrees very well with that from 1H nmr. The aromatic C-H bending region in the IR increases only marginally for the catalyzed Loy Yang oil (Fig. 1) but is markedly increased for the catalyzed Liddell oil (Fig. 2). The differences in the relative amounts of -OH stretchings are also reaffirmed by the amount of -C-O- IR spectral intensity, with the Liddell oils being less than the LY1277 oils, and the catalyzed Liddell oil being markedly reduced in the amount of -C-O- stretching while the LY1277 is only marginally reduced. Similarly the ^{13}C nmr also agreed with the 1H nmr data, indicating that the Aliphatic/Caromatic ratio decreases quite markedly between the LY1277 and Liddell oils (Fig. 3), but only slightly between the uncatalyzed and catalyzed oil from the same coal.

IR investigations of the residues revealed that the contribution of aliphatic $-CH_2-$, $-CH_3$ bending regions were greater in the catalyzed than in the uncatalyzed residues. CP-MASS ^{13}C nmr of LY1277 catalyzed residue (Fig. 4) showed it to have a lower aromaticity than the uncatalyzed residue, but still higher than the parent coal. For the Liddell case, however, both residues had the same aromaticity which again were higher than the parent coal. The data from the LY1277 residues indicates that the catalyst, may in fact be hydrogenating aromatic rings whilst dissolving the coal. Why this occurs only for LY1277 and not for Liddell may be due to the selectivity of the catalyst, displaying structural dependence for the chemically very different starting materials. The result is surprising considering the previous data on the oils and the similar aromaticities, but not if the differing structures of the two coals are taken into account.

Pyrolysis-Gas Chromatography of the residues and the parent coals reaffirms previous observations that the catalyst does alter the organic structure of the residues. A main observation is the loss of the alkane/alkenes in the catalyzed Liddell residue, while they are present in the uncatalyzed residue. This agrees with the marked increase in hydrocarbon gas production in the former. The pyrograms of the Loy Yang residues, although differing in some components between

uncatalyzed and catalyzed residues, are not dissimilar, differing mainly in relative quantities of components.

This paper has attempted to show that there are definite advantages and disadvantages associated with the catalytic/non catalytic liquefaction behaviour of coals possessing a wide variation in rank. The use of catalyst, while appearing to only increase the oil yield/conversion for Loy Yang coal, markedly upgraded the product from Liddell coal - thereby indicating a quite different mode of action (reflecting a structural dependence) in each case. The possibility that the mode of action and reactivity of the catalyst may be temperature dependent (as the oils were produced at two different temperatures) cannot be overlooked. It was not the purpose of this paper to investigate such a possible phenomena. Rather it was to show, and it clearly has, the problems that may arise in product quality and upgrading if the only criteria for liquefaction are oil yield and conversion based.

ACKNOWLEDGEMENT

M.G. Strachan acknowledges the award of a University of Melbourne Research Scholarship.

REFERENCES

- (1) Cudmore, J.F., *Fuel Proc. Technol.* 1977/1978, 1, 227.
- (2) Jackson, W.R., Larkins, F.D., Marshall, M., Rash, D. and White, N., *Fuel*, 1979, 58, 281.
- (3) Hatswell, M.R., Jackson, W.R., Larkins, F.P., Marshall, M., Rash, D. and Rogers, D.E., *Fuel*, 1979, 58, 783.
- (4) Jones, D.G., Rottendorf, H., Wilson, M.A. and Collins, P.J., *Fuel*, 1980, 59, 19.
- (5) Wilson, M.A., Rottendorf, H., Collins, P.J., Vassallo, A.M. and Barron, P.F., *Fuel*, 1982, 61, 321.
- (6) Strachan, M.G., Johns, R.B. and Yost, R.S., *Anal. Chem.* Submitted for publication.
- (7) Strachan, M.G., Chafee, A.L., Esdaile, R., Johns, R.B. and Yost, R.S., *Proc. 6th Aust. Coal Hydrogenation Workshop*, 1981, 7-16.
- (8) Downing, P.G., Ph.D. Thesis, University of Melbourne, 1980.
- (9) Charlesworth, J.M., *Fuel*, 1980, 59, 859.
- (10) Durie, R.A., *Coal Research in C.S.I.R.O.*, 1959, 6, 12.
- (11) Schwager, I., Farmanian, P.A. and Yen, T.F., *Adv. in Chem. Ser.*, 1978, 170, 66.

TABLE 1: PRODUCT DISTRIBUTION

Sample	Conversion %	Oil ^A yield	H ₂ O ^A yield	Residue	Gas ^A	H ₂ O/oil yield	gas/oil yield
LY1277 (uncat.)	60.30	45.92	6.52	40.72	6.84	0.14	0.15
LY1277 (cat.)	74.63	55.89	8.02	25.37	10.37	0.14	0.19
Liddell (uncat.)	62.22	59.57	1.48	37.78	1.17	0.03	0.02
Liddell (cat.)	91.75	54.71	8.25	8.25	29.53	0.15	0.54

A - g/100 g DAF coal

TABLE 2: ELEMENTAL ANALYSES

Sample	C	H	O* (DAF)	N	S	H/C	O/C	N/C	ASH
LY1277	65.66	4.48	31.34	0.80	0.20	0.819	0.358	0.010	<1.0
Liddell	80.1	5.9	10.90	2.03	1.0	0.883	0.102	0.022	28.1
<u>Total Oils</u>									
LY1277 (uncat.)	81.72	7.49	9.79	1.00	-	1.10	0.089	0.010	
LY1277 (cat.)	85.08	6.85	7.83	0.24	-	0.966	0.069	0.002	
Liddell (uncat.)	87.80	6.15	3.94	2.11	-	0.841	0.033	0.021	
Liddell (cat.)	90.71	6.53	1.53	1.23	-	0.863	0.013	0.015	
<u>Residues</u>									
LY1277 (uncat.)	80.13	4.98	16.93	1.05	-	0.746	0.159	0.011	3.0
LY1277 (cat.)	69.66	4.95	24.51	0.889	-	0.853	0.264	0.011	17.9
Liddell (uncat.)	82.73	4.85	9.97	2.45	-	0.704	0.090	0.025	25.6
Liddell (cat.)	63.18	4.64	29.38	2.81	-	0.881	0.349	0.038	72.6

*By difference

TABLE 3: CHEMICAL CLASS COMPOSITION OF TOTAL LIQUID PRODUCT (w/w % of oil)

Fraction*	LY1277		Liddell	
	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
A1	22.09	23.51	11.63	1.69
A2	0.86	0.68	2.72	1.91
A3	1.03	1.36	2.48	0.42
A4	6.72	5.62	2.48	0.84
A5	1.55	1.19	0.01	2.12
A6	1.38	1.87	2.72	1.06
B1	2.80	4.77	2.97	0.21
B2	9.00	9.03	50.50	15.25
TN	54.50	51.97	24.49	76.50
NPN	31.07	34.76	14.45	69.84
PN	23.43	17.21	10.04	6.66

A series - acidic fractions from resins

B series - basic fractions from resins

TN = Total neutrals, i.e., NPN + PN: NPN = Nonpolar neutrals;

PN = Polar neutrals.

*See Ref. 6.

TABLE 4: ¹H-NMR DATA ON TOTAL LIQUID PRODUCTS

Sample	¹ H nmr Data										Mw Data ^b		
	H ₀	H _α	H _{ar}	H _{OH}	$\frac{H_{ali}}{H_{ar}}$	$\frac{H_{ali}}{C_{ali}}$	$\frac{H_{ar}}{C_{ar}}$	f _a [†]	δG [†]	$\frac{H_{aru}^{\dagger}}{C_{ar}}$	n [†]	M \bar{n}	M \bar{w}
LY1277 (uncat.)	29.0	32.9	27.1	11.0	2.3	1.71	0.45	0.66	0.74	1.75 ^c	1.88	498	1049
LY1277 (cat.)	39.6	28.1	22.6	9.6	3.0	2.24	0.35	0.67	0.74	1.23	2.41	512	997
Lidell ¹ (uncat.)	35.7	23.4	31.2	9.6	1.9	2.49	0.43	0.75	0.54	0.58	2.52	379	758
Lidell ¹ (cat.)	21.3	29.3	45.1	4.3	1.1	2.27	0.60	0.78	0.35	0.76	1.73	169	240

† - Brown Ladner Method of ¹H nmr data analysis

b - GPC-HPLC method for molecular weight determination

c - High values due to high O/H ratio

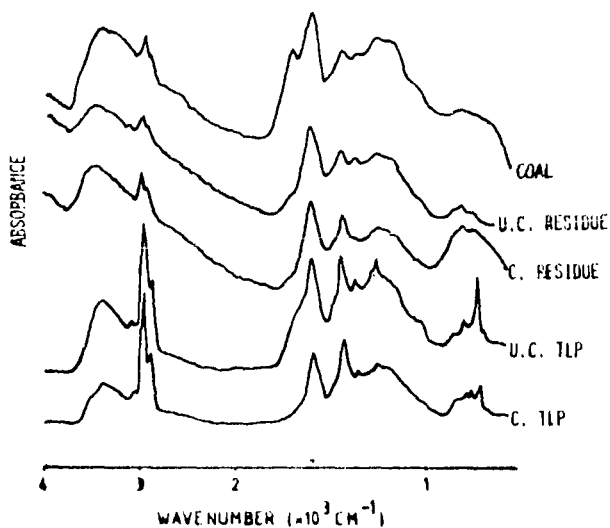


FIG. 1 I.R. SPECTRA OF LY1277 AND ITS LIQUEFACTION PRODUCTS

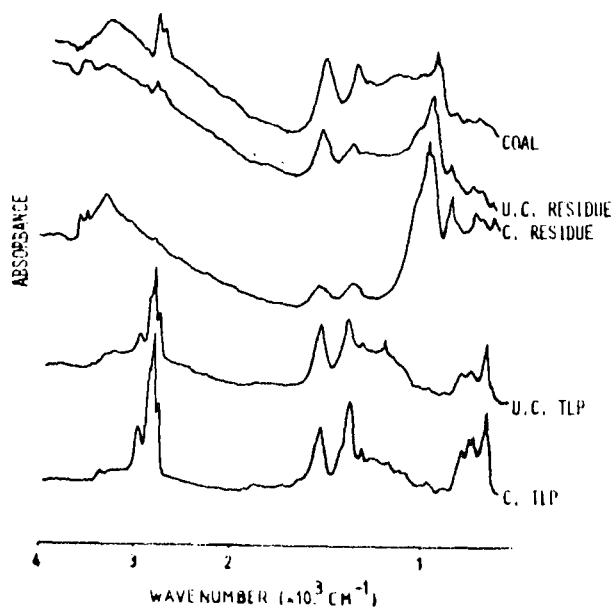


FIG. 2 I.R. SPECTRA OF LIDDELL AND ITS LIQUEFACTION PRODUCTS

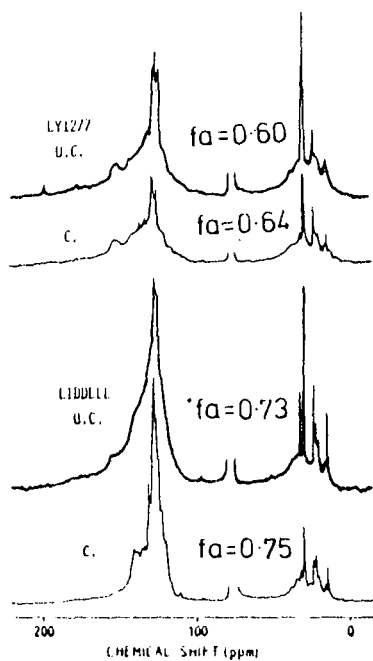


FIG. 3 25.0 MHz ^{13}C NMR OF TOTAL LIQUID PRODUCTS

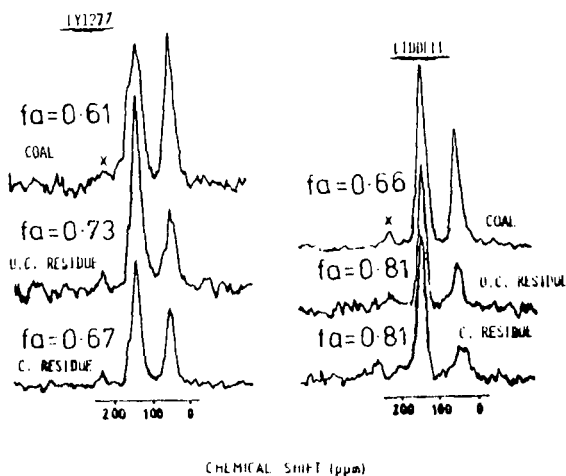


FIG. 4 SOLID STATE ^{13}C NMR OF COALS AND THEIR LIQUEFACTION RESIDUES

H-COAL® PROCESS MODELING AND SCALEUP

James B. MacArthur, Allen Li, and Anil S. Ambegaonkar

Hydrocarbon Research, Inc.
(A Subsidiary of Dynalelectron)
P. O. Box 6047
Lawrenceville, New Jersey 08648

ABSTRACT

H-Coal® Process commercial viability has been confirmed by a highly successful, 2-1/2 year demonstration program at the Catlettsburg, Kentucky, Pilot Plant. A major accomplishment was the confirmation of scale-up of the H-Coal® Process chemistry in the well-mixed ebullated-bed reactor system. This paper describes the H-Coal® Process Model developed from bench scale and PDU testing and its relationship to the Pilot Plant operations. Kinetics, hydrodynamics, and overall process simulation are described.

PROCESS BACKGROUND

The H-Coal® Process is a direct catalytic coal liquefaction process developed by Hydrocarbon Research, Inc. for conversion of coal into high-quality, clean liquid fuels⁽¹⁾. The process can be modified to produce a range of products from a heavy fuel oil to an all-distillate (C₄-650°F boiling range) syncrude. The novelty of the H-Coal Process resides in the use of the commercially proven ebullated-bed reactor in combination with other process steps to achieve C₄-975°F liquid product yields in the range of 40 to 55 weight percent on dry coal. Over twenty coal types have been evaluated in more than 70,000 hours of operation. The history development, and advances of the H-Coal® Process have been extensively documented. Some details of the process and HRI's ebullated bed reactor are appended to this paper.

H-COAL PROCESS SCALE UP

The development path for commercialization of the H-Coal Process is similar to that used by HRI for scale up of the commercial H-Oil™ residuum and heavy crude hydroconversion process. The H-Oil reactor system was successfully scaled up from the bench, through the PDU, followed by a pilot plant demonstration unit and finally to the commercial scale plant. The diameters of experimental reactors employed for collecting process, engineering and scale-up data are listed below. All reactors have operated at commercial design conditions.

	<u>H-Oil</u> <u>Reactor Diameter</u>	<u>H-Coal</u> <u>Reactor Diameter</u>
Bench Unit	3/4 in.	3/4 in.
Development Unit	8-1/2 in.	6 & 8-1/2 in.
Pilot Plant	4 ft. 6 in.	5 ft.
Commercial Plant	13 ft.	10-13 ft.

In addition, HRI has constructed two cold-flow reactor models for fluid dynamics studies and the development of improved reactor internals: a 6 in. x 12 ft glass column and a 5 ft x 24 ft. carbon steel vessel. These cold flow studies, combined with data collected from the various experimental units, have provided the information to scale the effects of equipment size, pressure and temperature on reactor fluid dynamics and vessel internals designs.

The performance of the H-Oil unit at the Kuwait National Petroleum Company's (KNPC) Shuaiba Refinery is evidence of this successful scale up technique. The KNPC H-Oil unit has two reactor trains, each operating on vacuum residuum at about 25,000 B/D. Both reactors have been operating since 1968.

The H-Coal reactor has been thoroughly tested in bench- and PDU-size systems and has recently completed a 2 1/2 year demonstration program at the Catlettsburg, Kentucky H-Coal Pilot Plant. The H-Coal Pilot Plant operation has achieved many significant results including:

- Confirmation of H-Coal process chemistry and equipment scale-up.
- Establishment of process mechanical operability and reliability in commercial-scale equipment
- Collection of engineering design and operating data on critical equipment
 - Slurry Preheater
 - Letdown valves
 - Slurry pumps
 - Reactor and internals
- Accumulation of about 7000 hours of on-coal operations with over 56,000 tons of coal processed.

H-COAL REACTOR IS WELL MIXED AND THERMALLY STABLE

To determine the degree of catalyst backmixing in an ebullated bed, a radioactively-tagged catalyst sample was charged to the PDU reactor in separate operations with Kentucky and Wyoming coals. The amount of tagged catalyst in the daily withdrawals and subsequent reactor catalyst bed dump was determined. The residence time distribution of catalyst in the ebullated-bed was then analyzed. A detailed discussion of the experimental procedures, and some of the test results were reported in the literature. The estimated reactor Peclet number reported by Bickel and Thomas⁽³⁾ for the Kentucky coal operation was 0.451. Using a modified dispersion model and taking into consideration the fluid dynamics during the catalyst addition and withdrawal operations, the Peclet number for the Wyoming coal operation was estimated to be 0.248 (detailed analysis to be published). These low Peclet numbers indicate that the catalyst mixing characteristics in the PDU ebullated-bed reactor approximated that of the CSTR.

The axial temperature variation in an ebullated-bed reactor is significantly smaller than that in a plug-flow (fixed-bed or moving-bed) reactor at the same conversion level. The axial temperature gradient (ΔT) in an ebullated-bed reactor can be estimated using the following expression:

$$\Delta T = \frac{-\Delta H_r}{\rho C_p} \frac{1}{1+R} (C_{Af} - C_{A1}) \quad (1)$$

where,

C_{Af} , C_{A1} = concentration of reactant in the feed and in the reactor outlet, respectively.

ΔH_r = heat of reaction

R = dimensionless constant related to recycle liquid/feed ratio and internal liquid backmixing. This constant ranges from 5-15 in ebullated-bed operations.

ρ , C_p = average fluid density and heat capacity, respectively.

The calculated temperature gradients from equation (1) are in agreement with PDU and Catlettsburg Pilot Plant data as shown below:

MEASURED VS. PREDICTED H-COAL REACTOR TEMPERATURE GRADIENTS

(Illinois No. 6 Coal, Burning Star Mine)

	<u>PDU-5</u>	<u>Catlettsburg</u>
Reactor Internal Diameter	0.71 ft.	5 ft.
Reactor Temperature	850°F	845-851°F
Reactor Pressure	2,700 psig	3,000 psig
<u>Reactor Temperature Gradient</u>		
Measured	16-20°F	11-18°F
Predicted	16°F	16°F

For a commercial-size H-Coal reactor operating at conditions similar to that of the Catlettsburg Pilot Plant, a temperature gradient of about 7°F was predicted. This lower reactor temperature gradient was due to increased backmixing in large size reactor. The same calculation procedure predicted temperature variations of 2-5°F in commercial H-Oil® reactors, which is consistent with commercial experience. The higher temperature gradients observed in H-Coal® reactors were caused by higher heat of reaction and lower ebullating recycle flow in the H-Coal® Process.

In plug-flow reactors, such as fixed beds and moving beds, the temperature gradient across the reactor for an exothermic hydrocracking reaction can be calculated using the following equation:

$$T_1 - T_f = \left(\frac{-\Delta H_r}{\rho C_p} \right) (C_{Af} - C_{A1}) \quad (2)$$

where subscripts f and l denote reactor feed and outlet conditions, respectively. Comparing equations (1) and (2), one can deduce that the axial temperature gradient in a plug-flow reactor is about one order of magnitude higher than that in an ebullated-bed reactor when both are operating at the same conversion level.

The well-mixed ebullating-bed reactor system enables commercial reactor systems to utilize the exothermal heat of reaction to preheat the H-Coal reactor feed. This enables the coal slurry preheater to operate at a low temperature ($\sim 700^{\circ}\text{F}$ at the Pilot Plant). No coke was found in the slurry preheater after 2-1/2 years of Pilot Plant operation because of the mild preheater severities. The H-Coal reactor system is energy-efficient, cost-effective, and has the potential for highest plant on-stream factors of any direct coal liquefaction process.

H-COAL PROCESS MODELLING

The H-Coal® Process has been successfully demonstrated on the bench scale with over 20 coal types including bituminous, sub-bituminous, lignite and brown coal.

The H-Coal® Process offers considerable product slate flexibility, ranging from an all-distillate syncrude to a maximum heavy fuel oil production. The H-Coal® Process meets these requirements through manipulation of key process variables including:

- Coal space velocity
- Catalyst type and replacement rate
- Hydrogen partial pressure
- Reactor temperature
- Recycle slurry composition

HRI has developed a tool to predict the effect of these key process variables on H-Coal yields and product qualities for Illinois No. 6 coal. The H-Coal® Process Simulator is a comprehensive computer model of the H-Coal reactor system at steady-state conditions. The Simulator includes recently updated correlations for H-Coal product qualities, reactor vapor/liquid equilibrium "K" values, and an H-Coal kinetic model. All reactor feed and effluent streams, reactor composition, and product yields and qualities are depicted. Procedures are contained in the Simulator for elementally balancing yields and calculating reactor slurry composition as a function of recycle slurry and recycle gas feed stream rates and compositions. The reactor slurry composition is an important parameter in the H-Coal kinetic model for predicting product yields.

HRI has developed a semi-empirical kinetic model based on a back-mixed reactor system. The conversion reactions are assumed to be irreversible. The reactions are first order except for preasphaltenes and asphaltene conversion. The reaction mechanism assumed is shown in Figure 1. Coal is made up of inert components (ash and inert organic material) and reactive components. The primary reactions involve the conversion of reactive coal to preasphaltenes and gases (including hydrocarbon and heteroatoms). Secondary reactions involve the conversion of preasphaltenes to asphaltenes, distillates (C_4 - 400°F , 400 - 650°F , and 650 - 975°F) and gases. Finally, in tertiary reactions, asphaltenes convert to distillates and gases, and distillates convert to lighter boiling components.

The kinetic model is incorporated into the H-Coal® Process Simulator. In the Simulator, empirical correlations are used to separate the distillate components into narrow (50°F) boiling range fractions. These components are utilized to obtain better estimates of reactor composition (through vapor/liquid equilibrium flash calculations), physical/chemical properties of the product streams, and for elemental balancing of the H-Coal® Process yields.

Table 1 summarizes the data base used to develop the H-Coal Kinetic Model for Illinois No. 6 Coal (Burning Star Mine). All process variables cover a wide range with the exception of temperature. The temperature effect has been modeled based on prior data obtained on a different Illinois coal (Monterey Mine).

TABLE 1. H-COAL KINETIC MODEL - RANGE OF DATA USED

COAL TYPE:	Illinois No. 6 (Burning Star Mine)
CATALYST:	HDS-1442A
NUMBER OF YIELD PERIODS:	140
PROCESS UNITS:	BENCH, PDU
<u>PROCESS VARIABLE RANGES</u>	
Coal Space Velocity	25 - 80 lb/hr/ft ³
Pressure	1450-2700 psia
Hydrogen Partial Pressure	1100-1900 psia
Temperature	840 - 852°F
Catalyst Age	0-600 hours
	0-3000 lb coal/lb catalyst
Operating Mode	Bottoms Recycle
Reactor Stages	Single

The H-Coal Kinetic Model components, correlating parameters, range of yield data, and standard deviations of the correlations are summarized in Table 2. Coal conversion is correlated as a function of coal space velocity, reactor temperature, and the concentration of reactive coal in the reactor. The Illinois coal is very reactive and coal conversion data covered a narrow range of 87-96 weight percent of MAF coal. Hydrogen partial pressure effects were not statistically significant. Although catalyst age and activity influence solvent quality, no catalyst impact on coal conversion could be correlated from available data. The standard deviation for the total bench and PDU data base was 1.2%.

TABLE 2. REVISED H-COAL KINETIC MODEL

<u>COMPONENT</u>	<u>FORM OF CORRELATION</u>	<u>RANGE OF YIELDS % MAF COAL</u>	<u>STANDARD DEVIATION</u>
Coal Conversion	F_1 (SV,T,C)	87-96	1.2
Preasphaltenes	F_2 (SV,T,AGE,H ₂ PP,C)	1.3-20	-
Toluene Conversion	F_1 - F_2		
Asphaltenes	F_3 (SV,T,AGE,H ₂ PP,C)	11-30	2.5
975°F ⁻ Conversion	F_1 - F_2 - F_3	45-80	2.0
650-975°F Liquid	F_4 (F_1 , F_2 , F_3 ,SV,C)	6-14	2.3
400-650°F Liquid	F_5 (F_1 , F_2 , F_3 , F_4 ,SV,C)	5-30	2.1
C ₄ -400°F Liquid	F_6 (F_1 , F_2 , F_3 , F_4 , F_5)	10-40	3.1
C ₁ -C ₃ Gas	F_7 (F_1 , F_1 , F_2 , F_4 , F_5)	5-15	1.7

Preasphaltene and asphaltene conversions were correlated as a function of coal space velocity, catalyst age, hydrogen partial pressure, reactor temperature, and reactor concentration. Statistical performance was significantly improved by correlating the toluene conversion (coal conversion minus preasphaltene yield) and 975°F⁺ conversion (coal conversion minus preasphaltene and asphaltene yield). This eliminated data scatter associated with small differences between large numbers. Standard deviations of 1.8% and 2.0% were achieved for the toluene conversion and 975°F⁺ conversion, respectively. Yields of distillates (C₄-400°F, 400-650°F, 650-975°F) were similarly correlated. The data, however, were more limited and data scatter more significant. Further data are required to confirm these reactions rate constants.

The H-Coal® Process Simulator includes empirical correlations of hydrogen consumption, and heteroatom (COx, H₂S, NH₃, H₂O) yields. Liquid product qualities are calculated by kinetic (for S,N) and empirical correlations.

The H-Coal® Process Simulator has been used extensively to predict H-Coal® Process performance over a wide range of operating conditions and to evaluate process improvements. Significant improvements have been made in increasing the recycle solvent boiling range (400°F⁺ to 600°F⁺) and extinguishing the heavy vacuum gas oil stream. This improves process economics when a transportation product slate is desirable.⁽⁴⁾ Also, recent studies have shown that the hydroclones used for preparation of recycle slurry oil may be eliminated in most cases without sacrificing liquid yields. The Simulator has been used to verify Pilot Plant performance.

H-COAL PILOT PLANT YIELDS PREDICTIONS CONFIRMED

The H-Coal Pilot Plant had a successful 131 day run with Illinois No. 6 and HDS-1442A catalyst (Run 8) during the second half of 1981. The run was conducted with daily catalyst addition and withdrawal to maintain a target catalytic activity. During this run, 19,200 tons of dried coal were processed with the reactor processing coal or oil slurry 100% of the time and coal fed for 72% of the time. The data obtained at the Pilot Plant are felt to be representative of what would be achieved in long term commercial operations.

Yield data were obtained in both September and a four-day material-balance period (October 29-November 2). The yield data obtained during the material-balance period were considered most representative due to lined-out H-Coal operations at steady-state conditions during this period.

Table 3 presents a comparison of yields obtained at the PDU scale with those obtained during the four-day material-balance period at the Pilot Plant for the Illinois No. 6 bituminous coal. Table 4 presents similar data for Wyodak sub-bituminous coal. These data show equivalent yields at the two scales and confirm the scaleup of H-Coal® Process chemistry. The H-Coal Kinetic Model and Process Simulator closely predicted the demonstrated Pilot Plant performance. These results provide confidence in HRI's ability to project commercial scale plant performance based on results obtained in bench and PDU units.

TABLE 3. H-COAL PROCESS CHEMISTRY SCALE-UP ILLINOIS NO. 6 COAL

<u>UNIT</u>	<u>PDU</u>	<u>PILOT PLANT</u>
Nominal Size, T/D	3.5	200
<u>YIELDS</u>	<u>PERCENT</u>	<u>PERCENT</u>
C ₁ /C ₃	10.68	11.77
C ₄ /400°F	18.74	22.41
400/975°F	28.33	25.27
975°F+ Residuum	19.00	21.26
Unconverted Coal	5.78	3.46
Ash	11.51	11.31
Total Distillate Oil	47.07	47.68
Residuum Plus Coal	24.78	24.72

TABLE 4. H-COAL PROCESS CHEMISTRY SCALE-UP WYODAK COAL

<u>UNIT</u>	<u>PDU</u>	<u>PILOT PLANT</u>		
Nominal Size, T/D	3.5	200		
<u>YIELDS</u>	<u>PERCENT</u>	<u>B/T</u>	<u>PERCENT</u>	<u>BTU</u>
C ₁ /C ₃	99.8	-	9.29	-
C ₄ /400°F	22.12	1.62	25.95	1.93
400/975°F	24.06	1.40	23.93	1.41
975°F+ Residuum	11.27	0.51	10.65	0.48
Unconverted Coal	10.72	-	9.12	-
Ash	8.84	-	9.13	-
Total Distillate Oil	46.18		49.88	
Residuum Plus Coal	21.99		19.77	

SUMMARY

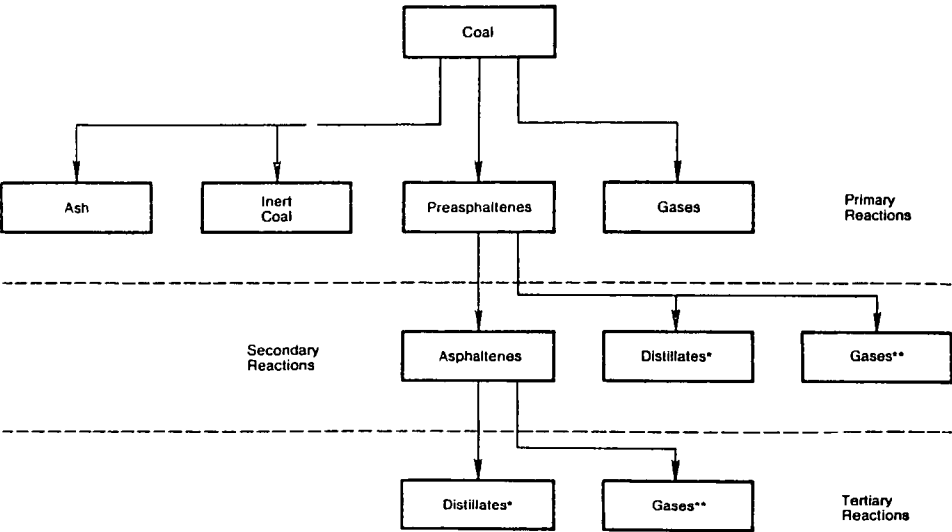
The H-Coal® Process follows the same successful development and scale up path used for the H-Oil Process. Results of reactor testing and modeling are in agreement with plant data, confirming that ebullated beds are well-mixed and highly stable. A kinetic model and overall process simulator have been developed and shown to accurately predict results from bench, PDU, and Pilot Plant scales. Pilot Plant results confirm scaleup of the H-Coal® Process chemistry. Data obtained in future bench and PDU units may be used with confidence for design of commercial scale plants.

REFERENCES

1. Eccles, R. M. and G. R. DeVaux, "Current Status of H-Coal® Commercialization", Winter National Meeting, AIChE, Orlando, Florida, March, 1982.
2. Li, A., and D. Lin, "Scaleup Performance and Thermal Stability Analysis of H-Oil and H-Coal Ebullated Bed Reactors", 32nd Canadian Society of Chemical Engineers Meeting, Vancouver, B.C., October, 1982.
3. Bickel, T. C., and Thomas, M. G., IEC Process Design and Development, Vol. 21, No. 3, July, 1982.
4. MacArthur, J. B., J. E. Duddy, A. S. Ambegaonkar, and A. V. Moomjy, "H-Coal Liquids-Upgrading Upstream or Downstream?" AIChE 1983 Spring National Meeting, Houston, TX, March, 1983.

FIGURE 1

H-Coal® Kinetic Model Reaction Mechanism



*Distillates are Separated into 3 Components Including C_4 /400°F Naphtha, 400/650°F Middle Distillate, and 650/975°F Heavy Distillate.

**Gases Include Hydrocarbons and Heteroatom Compounds.

APPENDIX

H-COAL PROCESS DESCRIPTION

Figure 1 presents a simplified flow diagram of the H-Coal Process. Coal is slurried with a process-derived oil, pumped to reactor pressure, mixed with hydrogen, preheated and fed to the reactor. There, coal, recycle oil, and hydrogen react in the presence of a catalyst. Depending on the process severity selected, the net product yield can be all-distillate material or, at low severities, a distillate and a heavy fuel oil. The reactor typically operates at temperatures of about 800-850°F and pressures of 2500-3000 psig. A portion of the reactor effluent is treated to reduce its solids content. Low-solid-content oil is recycled as a slurry oil for the coal. The balance of the liquid is fractionated to produce an all-distillate product. The vacuum residuum, containing nondistillate oils, unconverted coal, and ash, can be fed to a partial oxidation unit to produce the hydrogen for the process.

EBULLATED-BED REACTOR DESCRIPTION

Figure 2 is a sketch of the ebullated bed reactor which is the heart of the H-Coal reactor design. The reactor feed and recycle streams from the ebullating pump enter the bottom of the reactor. The liquid flow causes the catalyst bed to expand and fluidize. The catalyst remains in the bed. The reactor products, including the unconverted coal and ash solids, leave the bed and are separated for further processing. Because the catalyst is constantly in motion, a portion can be withdrawn and replaced to maintain high catalyst activity. On a daily basis, about one or two percent of the catalyst inventory is removed for this purpose. The ebullated-bed reactor system has over 30 unit-years of commercial operations in HRI's H-Oil® petroleum residuum hydroconversion process. The H-Coal® catalyst now being used has also been demonstrated commercially in H-Oil operations.

The ebullated-bed reactor allows intimate contact between catalyst particles, hydrogen, and the coal-oil slurry to achieve essentially isothermal reaction conditions and provide low constant reactor differential pressure. Other major advantages of the H-Coal reactor system are that:

- High liquid yields and qualities are achieved in the presence of a synthetic catalyst and are not dependent on the catalytic effect of coal ash.
- Continuous catalyst replacement controls deactivation, provides constant product quality, will permit continuous catalyst regeneration, and provides for high on-stream factors.
- Operating conditions can be varied to meet flexible product slate requirements.

Simplified H-Coal® Process Flow Diagram

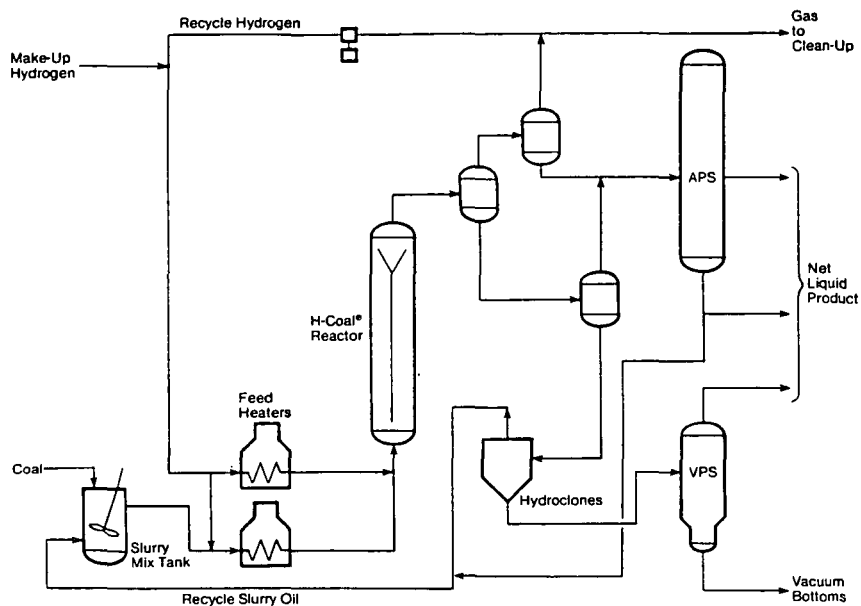
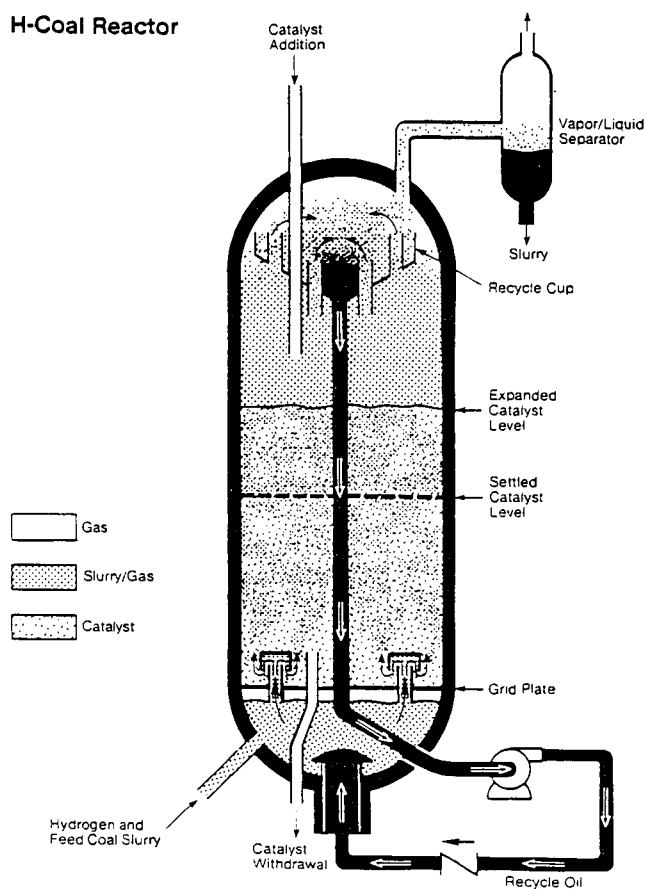


FIGURE A-2

H-Coal Reactor



HYDROGEN AND METHANE SOLUBILITY IN SRC-II COAL LIQUID

Fu-Xin Ding, Shiao-Hung Chiang and George E. Klinzing

Chemical and Petroleum Engineering Department
University of Pittsburgh
Pittsburgh, PA 15261

INTRODUCTION

The most important steps in coal liquefaction processes are the dissolution of coal in the hydrogen-laden solvent and the subsequent hydrotreating of the coal derived liquid. A small amount of methane is usually formed during coal liquefaction. Thus hydrogen and methane solubility data are essential for the design and operation of coal liquefaction reactors.

A number of investigators studied vapor-liquid equilibrium in binary and multicomponent systems of heavy hydrocarbon liquids and light gases, including hydrogen and methane.⁽¹⁻¹¹⁾ Only limited experimental data for methane-coal liquid and hydrogen-coal liquid mixtures have been reported in the literature.^(5,7) An attempt was made in this study to obtain solubility data in the binary system of hydrogen-coal liquid (SRC-III) and the ternary system of hydrogen-methane-coal liquid (SRC-II) under conditions comparable to those encountered in coal liquefaction processes. Two specially designed in-situ hydrogen probes were adopted for monitoring hydrogen concentration/partial pressure in both vapor and liquid phase.

EXPERIMENTAL

The experimental set-up and procedure used in this study are essentially the same as that described in previous papers.^(6,7) A schematic flow diagram of the equipment is shown in Figure 1.

A one-liter autoclave was used as the equilibrium cell. The autoclave is made of stainless steel and equipped with an automatic temperature controller capable of maintaining constant temperature within ± 1 K of the desired setting. A magnetic stirrer, driven by a variable speed motor, was installed in the autoclave. Two in-situ probes were used to measure the hydrogen partial pressure. The operating principle of these probes has been discussed elsewhere.⁽¹²⁾

Hydrogen and methane were supplied to the equilibrium cell from high pressure cylinders through gas feed lines. Liquid and gas samples can be withdrawn from the cell into the low pressure section. A Hewlett-Packard 5880A chromatograph system was used for sample analysis.

High pressure hydrogen (41 MPa) and methane (13 MPa) were used in this work with reported purity of 99.995% and 99.0%, respectively. The SRC-II coal liquid (supplied by the Gulf R&D Co.) was catalytically hydrotreated with Ni-Moly catalyst for four hours at 640°F.⁽⁷⁾

RESULTS AND DISCUSSION

Hydrogen-Coal Liquid Binary System. The hydrogen solubility data were obtained by measuring hydrogen partial pressure (using the in-situ probe) and by taking liquid samples at temperatures ranging from 420 to 681 K and total pressures from 4 to 11 MPa. Figure 2 shows the hydrogen solubility as a function of total pressure. When the total pressure is held constant, the hydrogen solubility increases with temperature to a maximum value and then decreases. The reason for this apparent solubility inversion is attributable to the rapid increase of coal liquid partial pressure with temperature, which causes a significant decrease in hydrogen partial pressure in the gas phase under constant total pressure. It can be shown that the hydrogen solubility increases monotonously with temperature if hydrogen partial pressure is held constant (Figure 3). In addition, hydrogen solubility data of this study are found to be in good agreement with the results reported by Lin et al.⁽⁵⁾ at temperatures below 550 K.

Hydrogen-Methane-Coal Liquid Ternary System. Experimental measurements were made at two temperatures, 591 K and 645 K, and at pressures up to 14 MPa. In order to determine the effect of methane on hydrogen solubility, methane partial pressure was varied from zero to 3.5 MPa. The experimental results are plotted in Figures 4 and 5. Under constant hydrogen partial pressure* and temperature, the hydrogen solubility decreases dramatically with an increase in methane partial pressure. For example, at 645 K and constant hydrogen partial pressure (9.52 MPa), hydrogen concentration in the liquid phase falls from 0.136 to 0.0387 mole fraction when methane partial pressure increases from zero to 3.0 MPa. The methane solubility versus its partial pressure is shown in Figures 6 and 7. The results indicate a linear relationship between methane solubility and its partial pressure at constant temperatures and constant hydrogen partial pressures. A study of the effect of hydrogen partial pressure on methane solubility is underway and the result will be presented in a future paper.

CONCLUSION

Hydrogen and methane solubilities have been experimentally obtained in the binary hydrogen-coal liquid (SRC-II) and ternary hydrogen-methane-coal liquid (SRC-III) systems at elevated temperatures and pressures. In the binary system, hydrogen solubility exhibits a temperature inversion at constant total pressure due to the strong dependence of coal liquid partial pressure on temperature. In the ternary system, hydrogen solubility is affected considerably by methane partial pressure at constant temperatures. The methane solubility exhibits a linear correlation with its partial pressure when hydrogen partial pressure is held constant.

ACKNOWLEDGEMENT

Funding of this work provided by U. S. Department of Energy, under the contract No. DE-AC22-80 PC33014, is gratefully acknowledged.

*The hydrogen partial pressure was accurately measured by the in-situ hydrogen probe.

REFERENCES

1. Legret, D., Richon, D. and Renon, H., J. Chem. Eng. Data, 1982, 27, 165-169.
2. Simnick, J. J., Sebastian, H. M., Lin, H. M. and Chao, K. C., J. Chem. Eng. Data, 1979, 24, No. 3, 239-240.
3. Lin, H. M., Sebastian, H. M. and Chao, K. C., J. Chem. Eng. Data, 1980, 25, 252-254.
4. Simnick, J. J., Lawson, C. C., Lin, H. M. and Chao, K. C., AIChE Journal, 1977, 23, No. 4, 469-476.
5. Lin, H. M., Sebastian, H. M., Simnick, J. J. and Chao, K. C., Ind. Eng. Chem., Process Des. Dev., 1982, 20, 253-256.
6. Sung, S., "Phase Equilibrium of Hydrogen/Coal Liquid System" Ph.D. Thesis (1981), Univ. of Pittsburgh, Pittsburgh, PA 15261.
7. Kara, M., Sung, S., Ding, F. X., Klinzing, G. E. and Chiang, S. H., Proceedings of Thermodynamics Symposium at the Second World Congress of Chemical Engineering, Oct. 4-9, 1981, Montreal, Canada.
8. Simnick, J. J., Liu, K. D., Lin, H. M. and Chao, K. C., Ind. Eng. Chem., Process Des. Dev., 1978, 17(3), 204-208.
9. Li, Y. H., Dillard, K. H. and Robinson, R. L., J. Chem. Eng. Data, 1981, 26, 200-204.
10. Simnick, J. J., Sebastian, H. M., Lin, H. M. and Chao, K. C., J. Chem. Eng. Data, 1980, 25, 147-149.
11. Brainard, A. J. and Williams, G. B., AIChE Journal, 1967, 13, 60.
12. Gala, H., Kara, M., Sung, S., Klinzing, G. E. and Chiang, S. H., AIChE Journal, 1981, 27, 159-162.

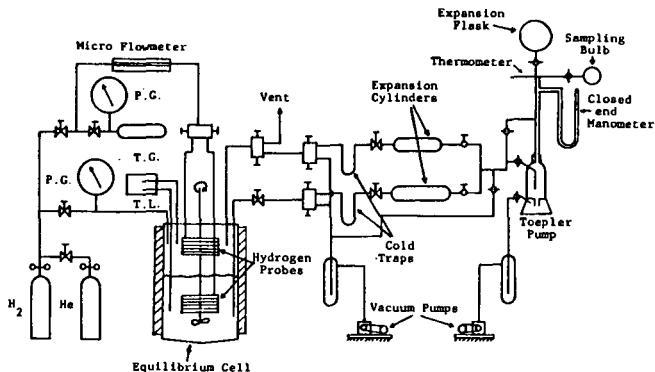


Figure 1 Schematic Diagram of the Experimental Set-up

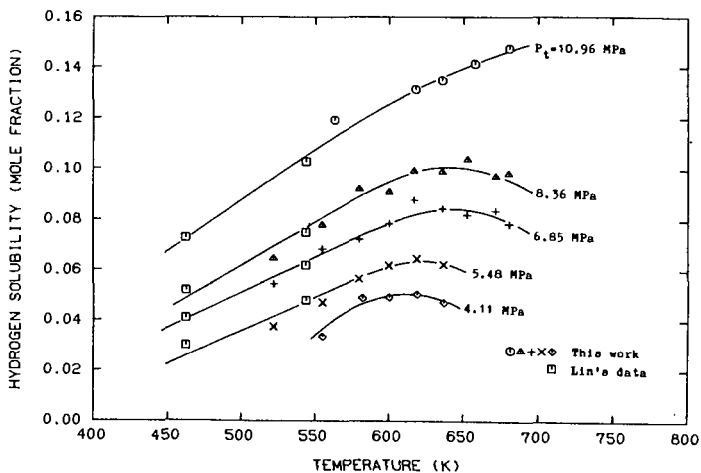


Figure 2 Hydrogen Solubility in SRC-II Coal Liquid vs. Temperature at Constant Total Pressure

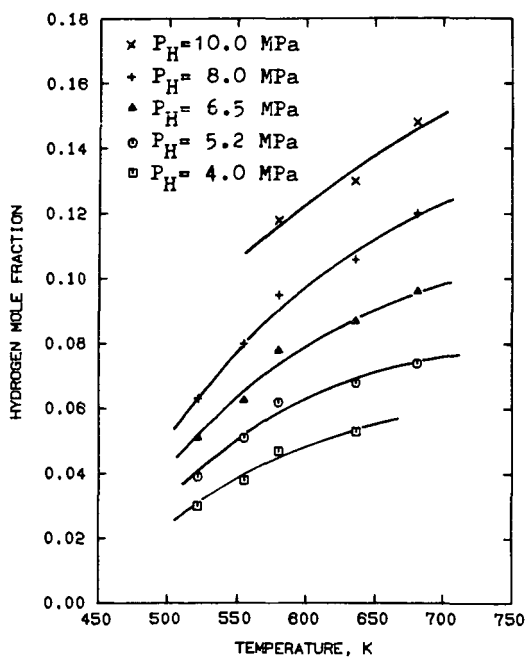


Figure 3 Hydrogen Solubility in SRC-II Coal Liquid vs. Temperature at Constant Hydrogen Partial Pressure

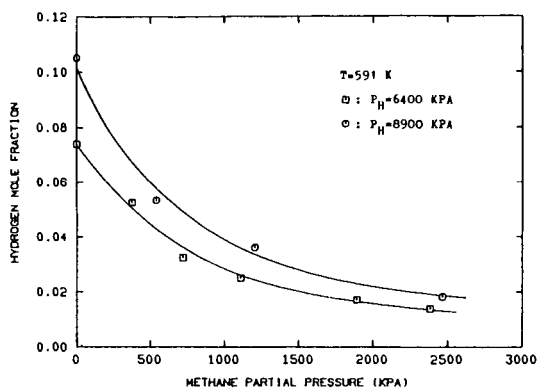


Figure 4 Hydrogen Solubility in SRC-II Coal Liquid vs. Methane Partial Pressure at 591 K

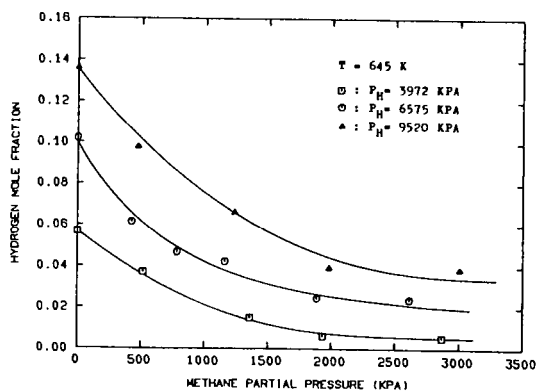


Figure 5 Hydrogen Solubility in SRC-II Coal Liquid vs. Methane Partial Pressure at 645 K

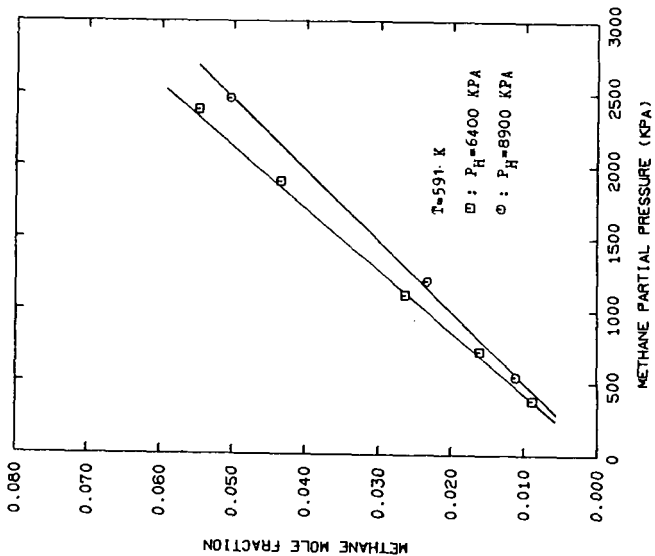


Figure 6 Methane Solubility in SRC-II Coal Liquid vs. Methane Partial Pressure at 591 K

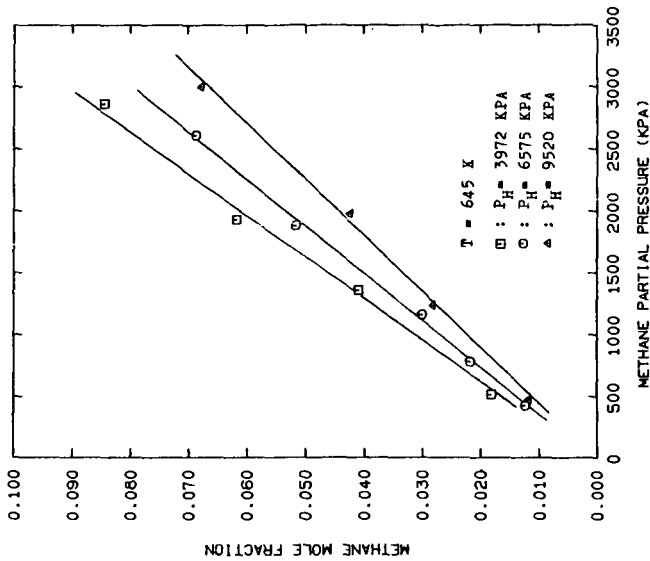


Figure 7 Methane Solubility in SRC-II Coal Liquid vs. Methane Partial Pressure at 645 K